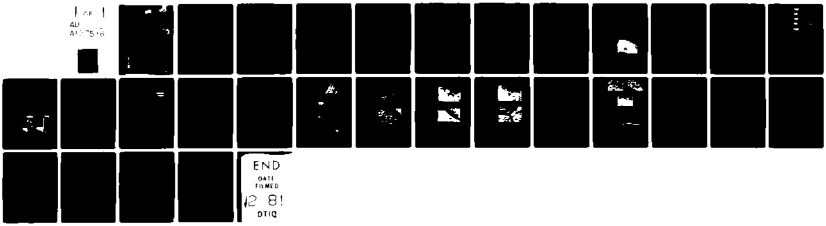
AD-A107 516 NEWCASTLE-UPON-TYNE UNIV (ENGLAND) F/G 11/6

THE OXIDATION AND CORROSION RESISTANCE OF NITRIDED IRON ALLOYS.(U)

JUL 81 K H JACK DA-ERO-79-G-0035

UNCLASSIFIED NL



[illegible]

[illegible]

1st Annual and Final Report
April [illegible] - March [illegible]

by

K.H. JACK

EUROPEAN RESEARCH OFFICE
United States Army
London W. 1, England

Grant Number DAERO-[illegible]

University of Newcastle upon Tyne, United Kingdom

Approved for public release; distribution unlimited

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AD-A107	3. RECIPIENT'S CATALOG NUMBER 516
4. TITLE (and Subtitle) The Oxidation and Corrosion Resistance of Nitrided Iron Alloys.		5. TYPE OF REPORT & PERIOD COVERED 1st Annual and Final Report April 1979 - March 1980
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) K. H. Jack		8. CONTRACT OR GRANT NUMBER(s) DAERO-79-G-0035
9. PERFORMING ORGANIZATION NAME AND ADDRESS The University of Newcastle upon Tyne Newcastle upon Tyne, NE1 7RU		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS IT161102BH57401
11. CONTROLLING OFFICE NAME AND ADDRESS USARDSG-UK, Box 65 FPO NY 09510		12. REPORT DATE 27 July 1981
		13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Approved for Public Release - Distribution Unlimited

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Nitrided steels, aqueous corrosion, potentiokinetic measurements, high temperature oxidation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Potentiokinetic measurements show that the corrosion resistance of austenitic Fe-34w/o Ni alloys containing Mo or Ti is increased by nitriding in NH :H gas mixtures to form respectively a homogeneous distribution of Mo N precipitates or a modulated structure of Ti-N clusters. Resistance to aqueous corrosion is also increased in alloys containing nitorgen in solid solution. A commercial nitrogen-alloyed steel, Nitronic 50, which has excellent corrosion resistance in the annealed condition is heavily attacked when tested after removal of nitrogen.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Cont./

High temperature oxidation studies of ferritic iron alloys in static air have been completed. No significant difference in weight gain is detected between alloys tested in the annealed, the nitrided or the nitrided and aged conditions for Fe-5w/o Mo and Fe-2.32w/o Cr alloys but superior oxide adhesion is observed on nitrided pure iron and alloys containing a dispersion of incoherent nitrides. Experiments on nitrided mild steel oxidised at 600°C demonstrate the resistance to fracture of oxides formed on nitrided alloys.

THE OXIDATION AND CORROSION RESISTANCE OF NITRIDED IRON ALLOYS

1st Annual and Final Report
April 1979 - March 1980

by

K.H. JACK

EUROPEAN RESEARCH OFFICE
United States Army
London W. 1, England

Grant Number DAERO-79-G-0035

University of Newcastle upon Tyne, United Kingdom

Summary

Potentiokinetic measurements show that the corrosion resistance of austenitic Fe-34w/o Ni alloys containing Mo or Ti is increased by nitriding in NH_3:H_2 gas mixtures to form respectively a homogeneous distribution of Mo_2N precipitates or a modulated structure of Ti-N clusters. Resistance to aqueous corrosion is also increased in alloys containing nitrogen in solid solution. A commercial nitrogen-alloyed steel, Nitronic 50, which has excellent corrosion resistance in the annealed condition is heavily attacked when tested after removal of nitrogen.

High temperature oxidation studies of ferritic iron alloys in static air have been completed. No significant difference in weight gain is detected between alloys tested in the annealed, the nitrided or the nitrided and aged conditions for Fe-5w/o Mo and Fe-2.32w/o Cr alloys but superior oxide adhesion is observed on nitrided pure iron and alloys containing a dispersion of incoherent nitrides. Experiments on nitrided mild steel oxidised at 600°C demonstrate the resistance to fracture of oxides formed on nitrided alloys.

Contents

I. INTRODUCTION

Experimental methods for nitriding iron and iron alloys to give any desired phase, cluster or solid solution have been established in extensive work at Newcastle (see Jack, 1974, 1975) and the chemistry and mechanical properties of the nitrided alloys are understood. However, resistance of nitrided alloys to oxidation and corrosion has received considerably less attention. The oxidation resistance of mild steel in simulated boiler flue-gas was shown by Hendry (1978) to be enhanced by a surface nitriding treatment and was attributed to refinement of the oxide grain size by nucleation on finely dispersed iron nitride particles and to the modification of the condensation process for vacancies at the metal-oxide interface. Coates & Hendry (1979) showed that nitriding of iron-titanium alloys also results in improved oxide adhesion compared to the un-nitrided alloy and that TiN particles act as nucleation sites for iron oxide in the same way as iron nitrides in mild steel. The first report under the present contract (Jack, 1979), now designated as "report J79", showed that nitriding resulted in small improvements in the resistance to oxidation in air of pure iron and iron-5w/o Mo alloys.

The criteria for resistance to aqueous corrosion are different from those for resistance to high-temperature oxidation although potentiokinetic measurements showed that nitriding and aging of Fe-5w/o Mo resulted in an order of magnitude decrease in current density compared with the un-nitrided alloy. The mechanism of corrosion was also found to change from general corrosion on annealed Fe-5w/o Mo alloys to pitting attack on nitrided alloys. Many claims have been made in the literature for the beneficial influence on aqueous corrosion of nitrogen in random solid solution and, in particular, on resistance to pitting attack (see for example Steenslund, 1969; Hartline, 1974; and Janik-Czachor et al. 1975). Truman et al. (1977) found that the effect of nitrogen (0.03 - 0.4w/o) is especially marked in a steel with 22w/o Cr and 3w/o Mo which showed increased resistance to pitting with increasing nitrogen content. Two manganese-nitrogen austenitic stainless steels (1CL.004BC and 1CL.016BC) were shown by Hochman (1977) to have superior resistance to intergranular and pitting corrosion and were suggested as suitable alternatives to AISI 304L and 316L (18Cr-8Ni types with molybdenum). The Armco Steel Corporation Nitronic series of austenitic stainless steels is a further example of this type of nitrogen-alloyed steel. Nitronic 50 combines high strength and toughness from sub-zero up to elevated temperatures with good corrosion resistance and is also claimed to exhibit high resistance to crevice corrosion. The alloy is currently used in marine applications where a combination of corrosion resistance and mechanical strength is essential.

The present report gives the results of potentiokinetic measurements in tap water carried out on nitrided austenitic alloys containing molybdenum and titanium and also on Armco Nitronic 50 in natural sea water. The results show that the presence of nitrogen as substitutional -interstitial solute atom clusters (non-random solid solution) in the laboratory alloys and in random solid solution in the commercial steel results in a decrease in corrosion. Oxidation studies on nitrided iron, mild steel, iron-molybdenum and iron-chromium alloys in air at 500°C are also reported and the results are discussed in terms of the integrity of the oxide film and the condensation process for vacancies formed during oxide growth.

II. SCIENTIFIC WORK

II.1 Corrosion resistance

Studies of aqueous corrosion can be carried out by several different techniques varying from simple weight loss measurements to complex electrochemical observations. Initial attempts were made to use linear resistance polarisation measurements. These are relatively simple and are widely used in the chemical industry to monitor corrosion. However, the commercial equipment employed gave inconsistent results that could not be correlated with the values expected for standard alloys. Potentiokinetic measurements of anodic polarisation were therefore used to study relative rates of corrosion. Measurements were made in tap water and natural sea water using the system shown in Figure 1 where the working electrode (WE) is the specimen, the auxiliary electrode (AE) is platinum, and the reference electrode (RE) is a saturated calomel electrode (SCE). The equipment could be programmed to sweep through a range of potential at a predetermined rate and log-current versus potential curves were plotted.

Potentiokinetic measurements on ferritic Fe-5w/o Mo alloys reported in J79 showed that the presence of Mo-N clusters or small nitride precipitates improved the resistance to corrosion in tap water. Similar measurements have been carried out on austenitic alloys Fe-34w/o Ni-3w/o Mo and Fe-34w/o Ni-2w/o Ti. The microstructure of the nitrided Mo-containing alloy consists of a homogeneous dispersion of Mo_2N precipitates in an austenitic matrix and the titanium alloy has a "modulated" microstructure of Ti-N clusters (see Figure 2) similar to that described by Driver et al. (1979) for nitrided Fe-34w/o Ni-2w/o V alloys. The alloys were tested in the annealed condition and after nitriding in $10NH_3:90H_2$ at 700°C; results are shown in Figures 3 and 4. The austenitic alloys behave in a similar manner to ferritic Fe-5w/o Mo alloys (see J79) and corrode after nitriding to a smaller extent than in the annealed state; that is, the current density at positive potentials is lower after nitriding. Pitting was

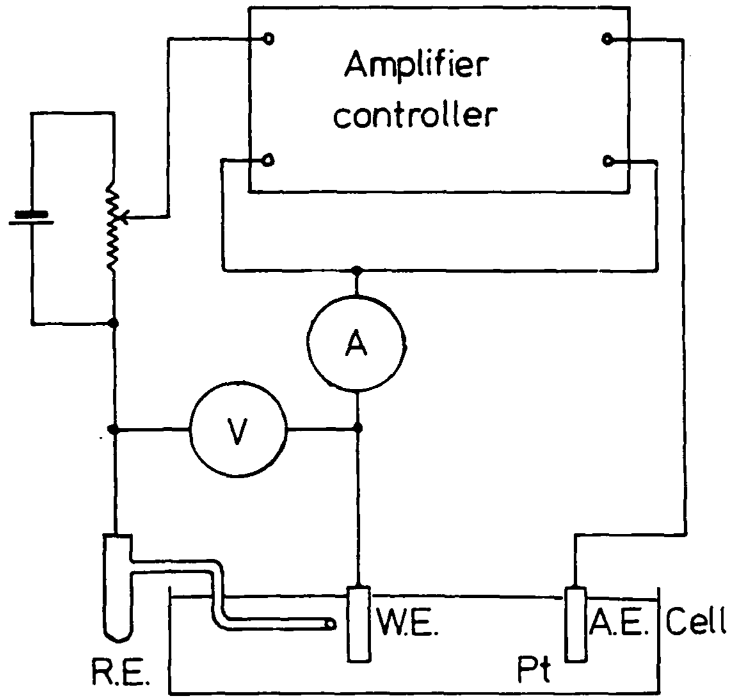


Figure 1. Schematic diagram of the potentiokinetic test equipment

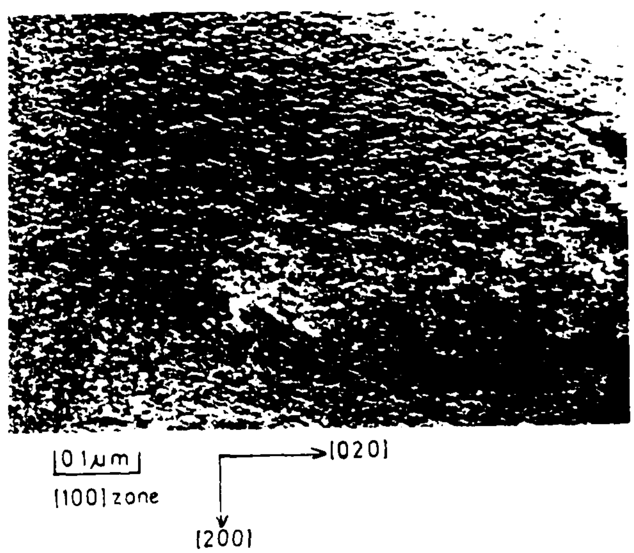


Figure 2. The microstructure of Fe-34w/o Ni-2w/o Ti nitrided in $10NH_3:90H_2$ at 700°C

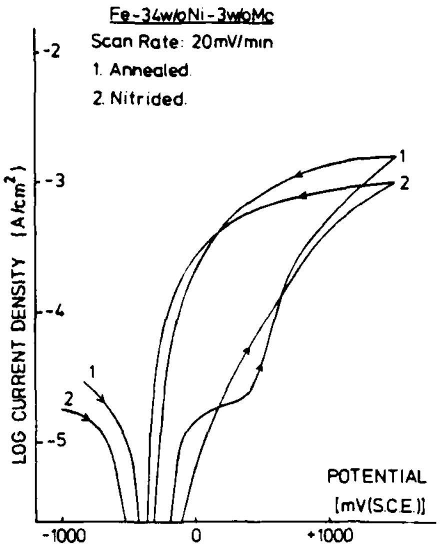


Figure 3. The effect of nitriding on the anodic polarisation behaviour of Fe-34w/o Ni-3w/o Mo in tap water

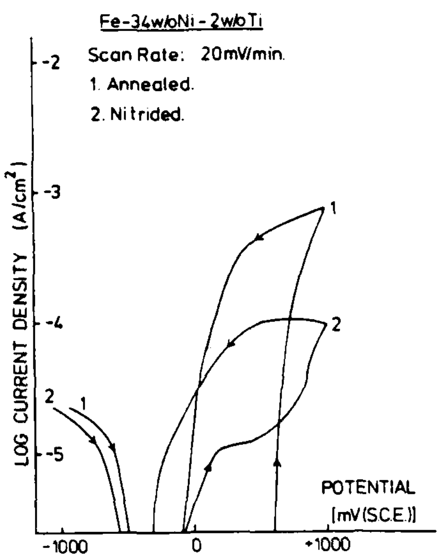


Figure 4. The effect of nitriding on the anodic polarisation behaviour of Fe-34w/o Ni-2w/o Ti in tap water

observed on all specimens and the pits began to grow at approximately 1.0 volt for the alloy containing titanium and at 1.2 volts for the molybdenum alloy.

The nitrided alloys reported above and that reported previously in J79 are laboratory alloys in which nitrogen is present as clusters or precipitates in a matrix containing some nitrogen in random solid solution. It is impossible to separate the influence on corrosion resistance of nitrogen in solid solution from that of a distribution of particles because aging of nitrogen in solid solution occurs even at room temperature. The commercial steel Nitronic 50 has the composition:

C	Si	Mn	Cr	Ni	Mo	Nb	V	N
0.04	0.48	5.00	21.60	12.43	2.17	0.16	0.17	0.25w/o

in which it is possible (Mallick, 1979) to retain all the nitrogen in solid solution by a solution anneal and quenching treatment. The as-received steel contains precipitates of $Cr_{23}C_6$, Cr_7C_3 and Z-phase Cr_2Nb_2N. Figure 5 shows that solution treatment above 1000°C dissolves the precipitates and after 1h at 1150°C no precipitate reflections are detected on X-ray photographs. Two sample conditions were prepared for comparative corrosion tests. The first samples were completely denitrided by holding at 1150°C in hydrogen and then quenching. The second set of samples was held for 1h at 1150°C in a gas mixture of $95N_2:5H_2$ and then quenched in order to maintain the original concentration of nitrogen (0.25w/o) in solid solution, composition of the gas mixture being calculated from Turkdogan & Ignatowicz (1958). Potentiokinetic corrosion tests were then carried out (Figure 6) to compare (1) denitrided Nitronic 50 with (2) Nitronic 50 containing nitrogen in solid solution. The denitrided alloy has a considerably higher current density and therefore greater rate of corrosion than the nitrogen-alloyed steel. A similar potentiokinetic study of Nitronic 50 and three unspecified high-nickel alloys has been carried out by Bridon Wire Limited and the results, shown in Figure 7, are in good agreement with the present study.

The observed increase in corrosion resistance of the nitrogen-containing steel was confirmed by further tests at constant potential. Specimens were subjected to a voltage sweep up to +1.32 volts in order to initiate corrosion and the potential then reversed and held constant at +0.8 volts for 20h. The denitrided specimen corroded severely and had a weight loss after the experiment of 14% while the nitrogen-alloyed steel was only slightly attacked by crevice corrosion around an O-ring seal on the sample holder and suffered a weight loss of only 0.5%. The difference in attack is clearly shown in Figure 8.

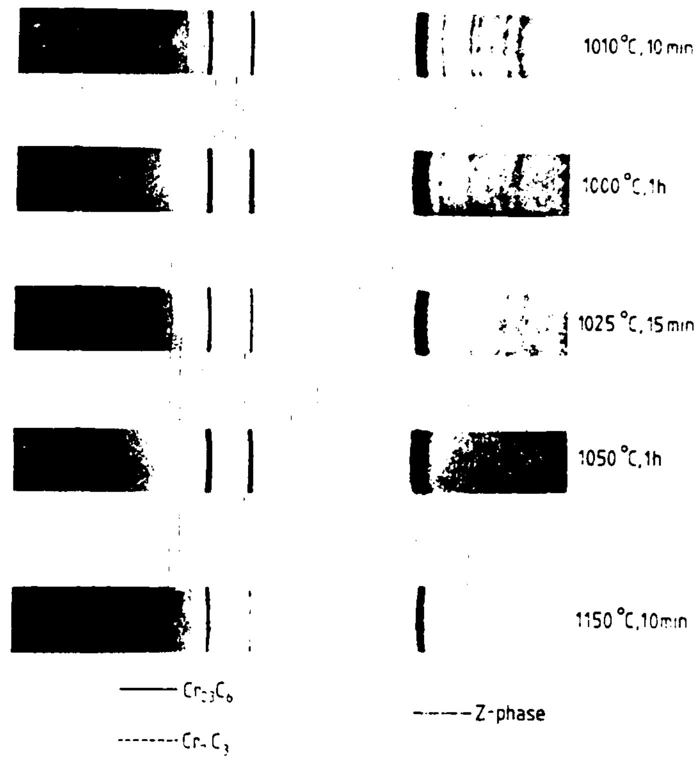


Figure 5(a) X-ray powder photographs showing the phases present in Nitronic 50 heat treated at 1000 to 1150°C

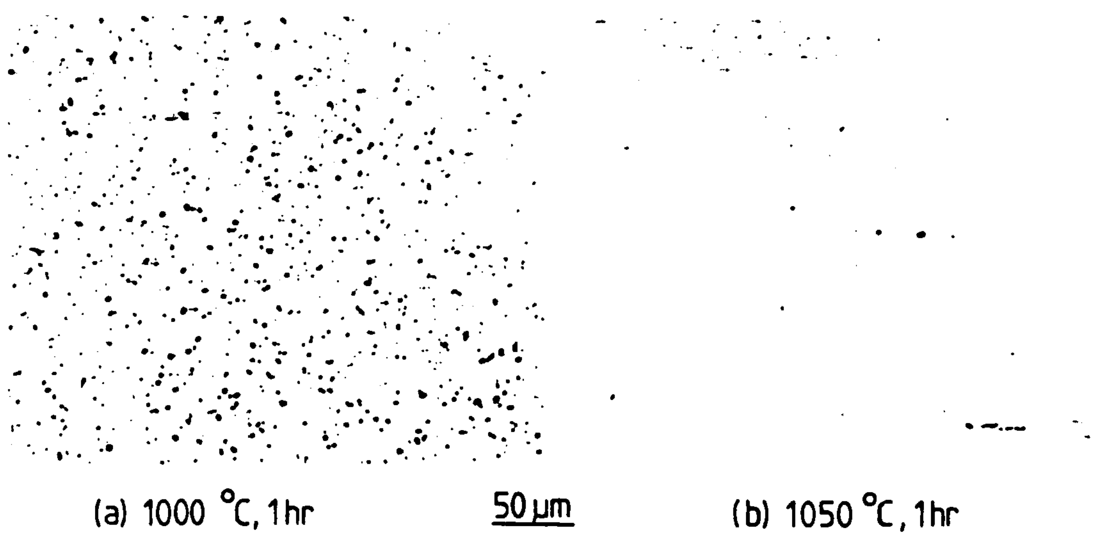


Figure 5(b) Optical micrographs of heat treated Nitronic 50

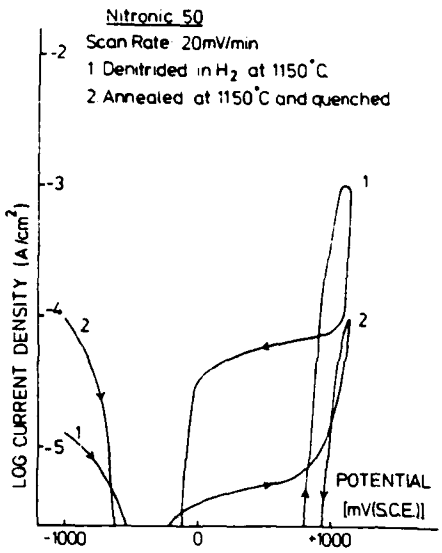


Figure 6. The effect of nitriding on the anodic polarisation behaviour of Nitronic 50 in natural sea water

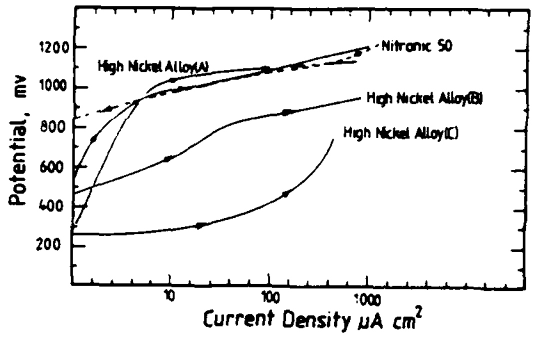


Figure 7. Anodic polarisation behaviour of Nitronic 50 and high nickel alloys (Bridon Wire Limited)

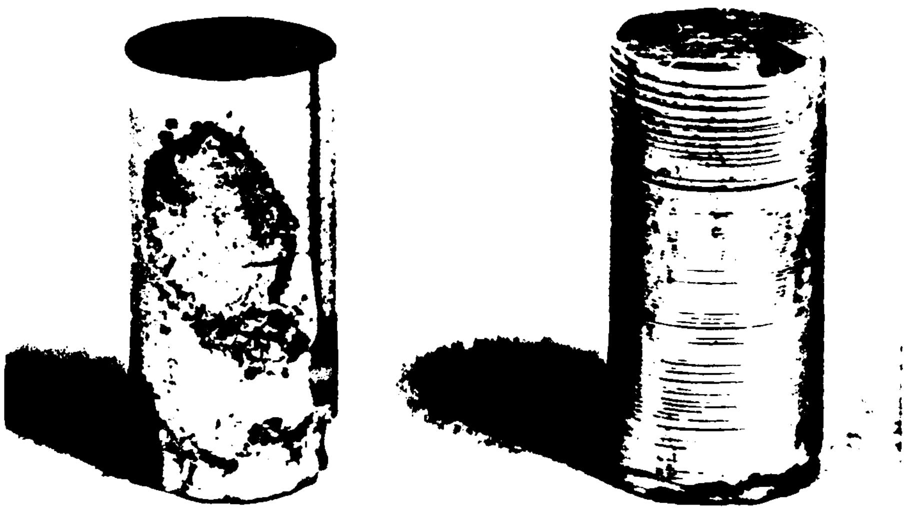


Figure 8. Specimens of (a) denitrided and (b) annealed and quenched Nitronic 50 after 20h in natural sea water at +0.8 volts (SCE)

II.2 Oxidation resistance

Report J79 presented results of preliminary oxidation experiments in dry, static air on pure iron and Fe-5w/o Mo alloys. These tests have now been completed together with experiments on the oxidation of iron-chromium alloys and mild steel. The oxide morphologies were studied by optical microscopy and scanning electron microscopy (SEM).

Thermogravimetric measurements have been carried out on annealed, nitrided and nitrided and aged Fe-5w/o Mo alloys during oxidation. Specimens were nitrided in $7NH_3:93H_2$ at 580°C to form Mo-N clusters (Driver et al., 1972) and some samples were then overaged by heating to 720°C for 1h to transform the clusters to the equilibrium precipitate, η-Fe_3Mo_3N. X-ray powder photographs of the samples used for oxidation experiments are shown in Figure 9. The results of oxidation in air at 480°C are shown in Figure 10. The observed weight gains are extremely variable as shown by comparing the upper curve of Figure 10 (reproduced from Figure 2 of report J79) with the lower solid line obtained from an identical but separate experiment. The differences between annealed, nitrided and aged alloys are therefore not sufficiently large to be meaningful. Metallographic studies show however that oxide adherence on nitrided and on nitrided and aged samples is greater than on the annealed alloys. Samples of pure iron were nitrided in $7NH_3:93H_2$ at 700°C and air-cooled to produce an austenite and martensite ($\gamma + \alpha'$) microstructure which transforms to ferrite and Fe_4N ($\alpha + \gamma'$) on reheating to 480°C (Coates & Hendry, 1979). Specimens of iron and the as-nitrided alloy were oxidised in static air for periods up to 1200h and the results of weight gain measurements, shown in Figure 11, confirm the preliminary results reported in J79. Nitrided iron has only a slightly greater resistance to oxidation than annealed iron but metallography shows that the adherence of the oxide layer is significantly greater on nitrided specimens. This is also observed with Fe-Mo and other nitrided alloys. Thus, thermogravimetric measurements alone do not present a complete picture of the oxidation process and must be combined with careful metallographic observations.

Similar experiments to those on Fe-5w/o Mo alloys were carried out on Fe-2.32w/o Cr to determine whether nitriding affects the oxidation resistance of a steel containing an active oxidation-resistant substitutional solute. Samples of Fe-2.32w/o Cr (i) annealed, (ii) nitrided ($10NH_3:90H_2$, 575°C) and (iii) nitrided and aged ($10NH_3:90H_2$, 575°C + 650°C for 1h) were oxidised at 500°C in static air. The differences in weight gain during oxidation (Figure 12) are small but significant improvements in oxide adherence on the nitrided alloys were observed. As similar improvements in oxide adherence had been noted in iron and in Fe-Mo alloys, a detailed examination was made by SEM of the oxide on Fe-Cr alloys. Figure 13 shows an SEM micrograph of the oxide on a nitrided sample of Fe-2.32w/o Cr. On annealed and oxidised alloys

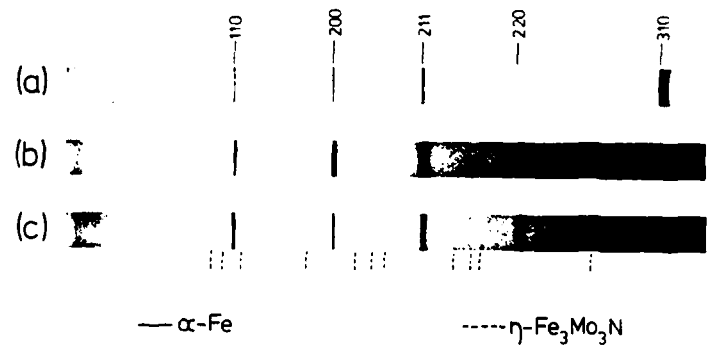


Figure 9. X-ray powder photographs of Fe-5w/o Mo (Co,Kα) (a) annealed, (b) nitrided in $7NH_3:93H_2$ at 580°C, and (c) nitrided as (b) and aged for 1h at 720°C

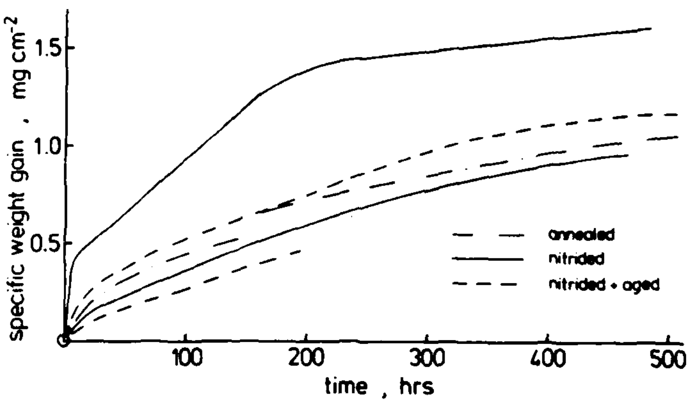


Figure 10. Oxidation curves of Fe-5w/o Mo alloys oxidised in air at 480°C

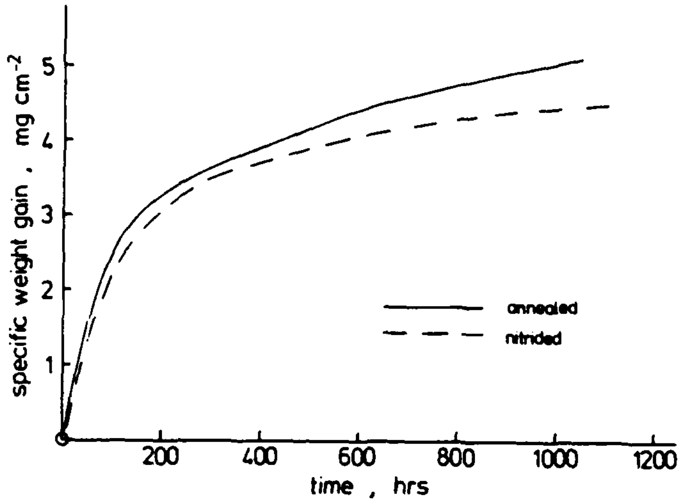


Figure 11. Oxidation curves of annealed and of nitrided iron ($7NH_3:93H_2$ at 700°C) oxidised in air at 480°C

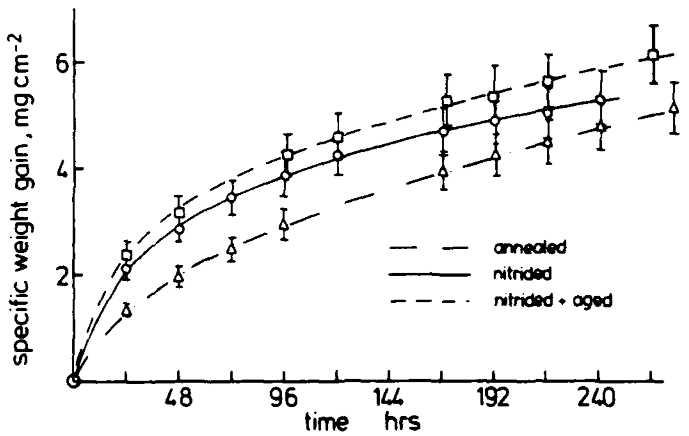


Figure 12. Oxidation curves of Fe-2.32w/o Cr alloys oxidised in air at 500°C

few areas of oxide adhering to the metal surface were found but the structure of the oxide was similar to that of Figure 13 with a duplex inner scale and a thin outer oxide layer. Similar duplex scales were also observed on aged samples. The oxide films were stripped from the metal substrate using a solution of 12w/o iodine in methanol and examined by X-ray diffraction and SEM. X-ray diffraction (Figure 14) shows that three phases are present in all three alloy conditions: haematite, Fe_2O_3 (outer thin layer); magnetite, Fe_3O_4 (main scale layer); iron-chromium spinel, $FeCr_2O_4$ (inner scale layer). The photograph of the oxide from the annealed specimen has had a longer exposure than the other two but the relative intensities of the reflections from the three oxide phases are similar in all three photographs showing that the relative amounts of the three phases are approximately the same.

Figure 15 shows the underside of the oxide removed from annealed Fe-2.32w/o Cr. 15(a) shows that the oxide clearly replicates the grain size of the substrate. The oxidation rate is influenced by the orientation of the matrix, as illustrated by the varying depths of the oxide surface in different grains. The oxide is covered in small voids as seen at the higher magnification 15(b). The areas corresponding to the grain boundaries of the matrix show no evidence of enhanced or suppressed oxidation. Figure 16 shows the underside of an oxide film stripped from the metal after nitriding to give a clustered matrix and 16(a) again shows that it replicates the substrate grain size; 16(b) is the same at higher magnification. The voidage at the surface is even more pronounced than on the annealed specimen. The matrix grain-boundary region shows extensive outgrowths which are remnants of CrN precipitated in the substrate grain boundaries that have not been dissolved during the stripping process. The presence of the CrN indicates that stripping has occurred at the metal/oxide interface and not at the interface between the two oxide layers. In Figure 17, which shows the oxide from the nitrided and aged alloy, the grain size of the matrix is again clearly reflected in the morphology of the oxide (17a) and at higher magnification (17b) the surface of the oxide appears much smoother than in the previous specimens and shows little voidage; the grain-boundary regions again contain CrN. Dispersed incoherent CrN precipitates thus act as vacancy sinks eliminating metal/oxide interfacial voidage, whereas coherent Cr-N clusters do not. The evidence of the present work and related published results (Hendry, 1978; Coates & Hendry, 1979) indicate that the role of nitride particles is to act as nucleation sites for oxide formation and so gives a fine grain size in contact with the metal surface. In addition, the condensation of vacancies at the oxide/metal interface is decreased, possibly by annihilation of vacancies at the nitride particles, and this decreases the probability of condensation to form voids.

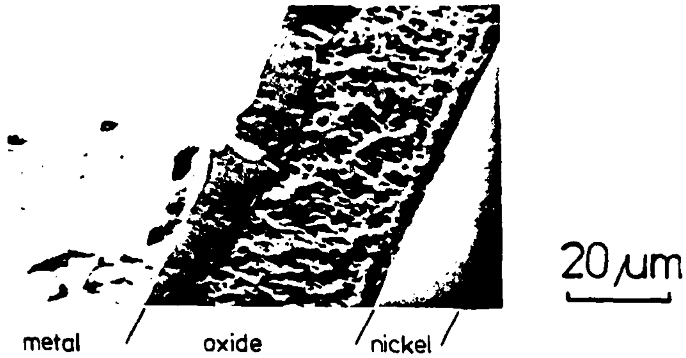


Figure 13. SEM micrograph of Fe-2.32w/o Cr nitrided in $10NH_3:90H_2$ at 575°C and oxidised in air for 240h at 500°C

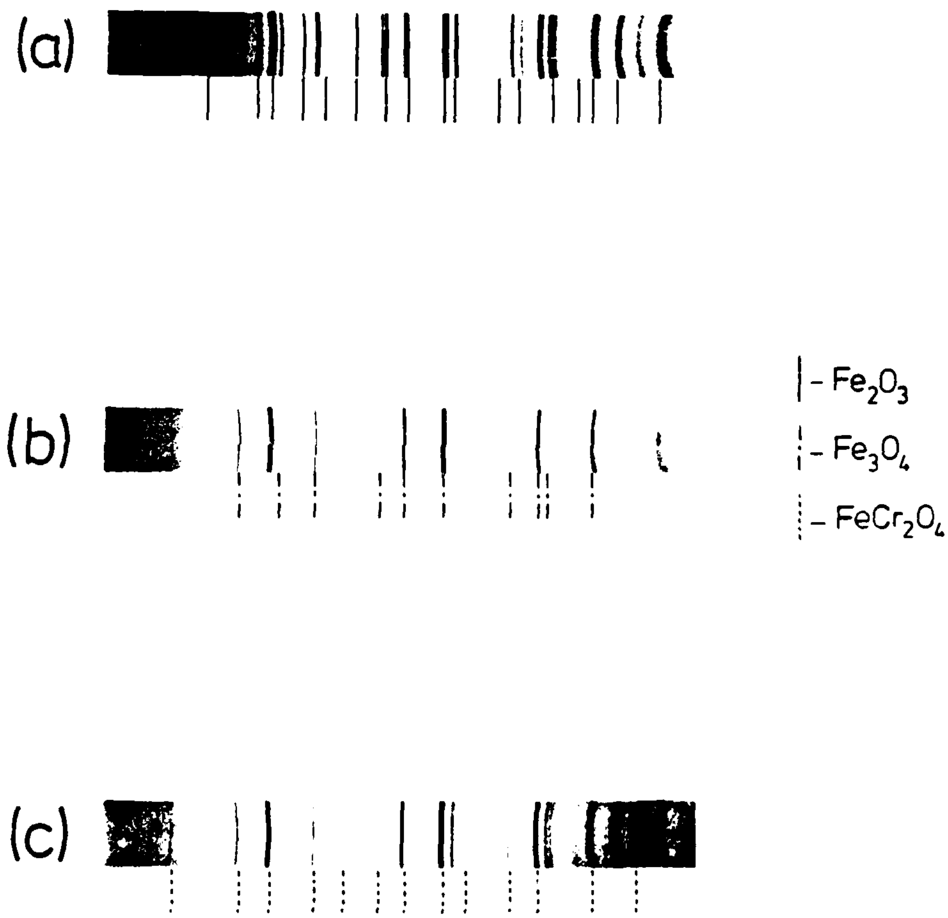


Figure 14. X-ray powder photographs of oxides from Fe-2.32w/o Cr specimens oxidised in air for 300h at 500°C, (a) annealed, (b) nitrided in $10NH_3:90H_2$ at 575°C, and (c) nitrided as (b) and aged for 6h at 650°C

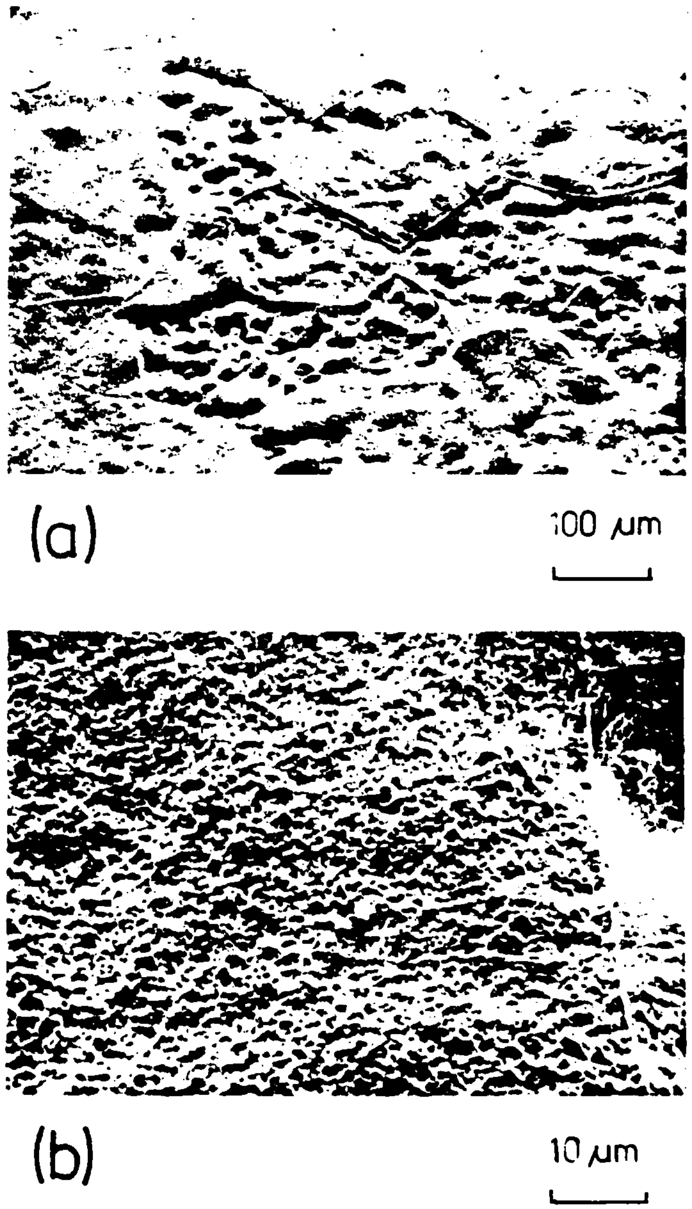


Figure 15. SEM micrographs of oxide stripped from annealed Fe-2.32w/o Cr oxidised in air for 300h at 500°C

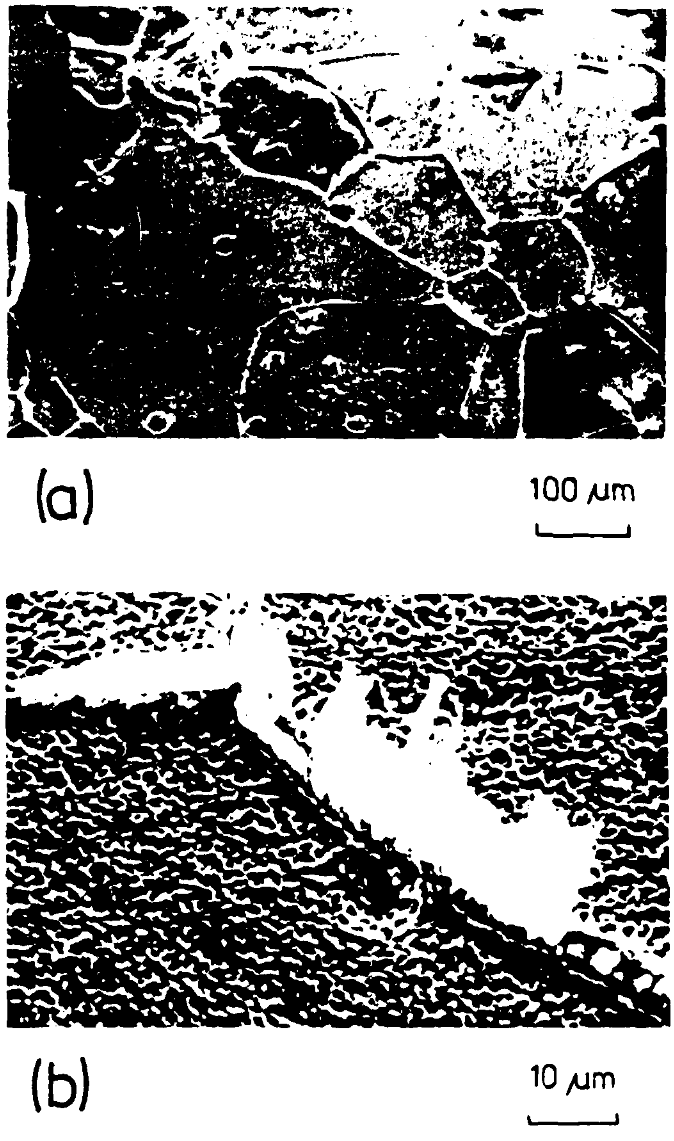


Figure 16. SEM micrographs of oxide stripped from nitrided Fe-2.32w/o Cr oxidised in air for 300h at 500°C

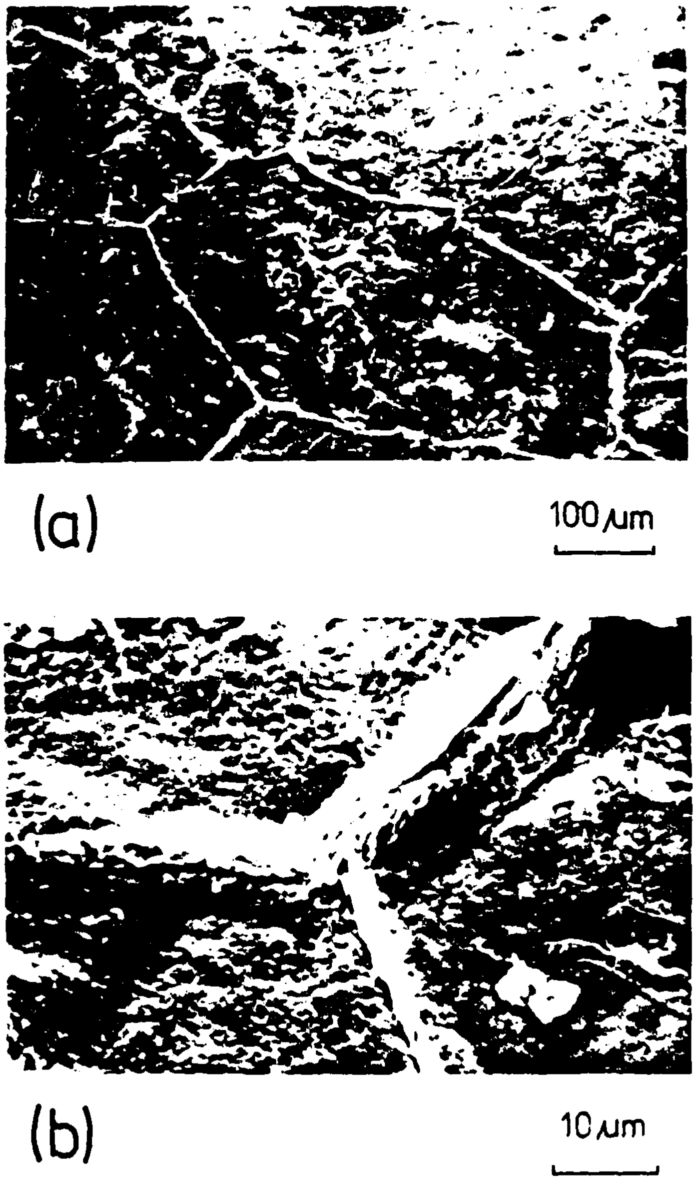


Figure 17. SEM micrographs of oxide stripped from nitrided and aged Fe-2.32w/o Cr oxidised in air for 300h at 500°C

The improved adherence of the oxide on nitrided alloys is at variance with the observed oxidation weight gains of alloys in the nitrided and un-nitrided conditions. The rates of weight gain are the same for all alloys whether they contain dispersed nitrides, clusters, or are un-nitrided. This is thought to be due to the reduction in interfacial voidage in dispersoid-containing alloys, allowing unrestricted cation transfer from the metal to the oxide. Thus, although interfacial adhesion is improved, the oxidation conditions are insufficiently aggressive to cause spalling of the oxide on un-nitrided alloys and consequently no obvious benefit of improved adhesion is observed by weight gain measurement.

Stresses imposed on oxide films by cooling to room temperature are much greater than those experienced isothermally at oxidation temperature and the oxide layer on annealed samples is found to be heavily cracked and separated from the metal substrate while that on nitrided and aged alloys is quite intact. It was shown by Coates & Hendry (1979) that the dispersed nitride particles act as nuclei for an extremely fine grained oxide layer which has a higher fracture strain than a coarse-grained oxide. The improved mechanical properties of oxide on nitrided alloys has also been demonstrated in the present work by oxidation experiments at 600°C on nitrided mild steel. Wustite (FeO) is stable in air above 570°C and comprises the greater proportion of the scaling layer on iron oxidised above this temperature with only a thin outer layer of Fe_3O_4 and Fe_2O_3. Figure 18(a) shows the morphology of the underside of the oxide removed from a specimen of nitrided mild steel ($5NH_3$:$95H_2$, 700°C) oxidised at 600°C for 650h. The oxide is convoluted and contains small angular particles in the valleys while the surface of the metal substrate (Figure 18(c)) is relatively smooth. Figure 18(b) shows the angular particles and Figure 19 is a schematic diagram of the oxide cross-section. The tendency for oxide buckling during oxidation is noted by several authors (Howes, 1968, 1969; Tien & Pettit, 1972) and is generally associated with thermal strain gradients but in the present case of isothermal oxidation it is believed to arise from differential growth stresses at the magnetite/wustite interface. The crystalline morphology of the angular particles formed within the voids can be produced only by (a) vapour phase transport of the reactants (Fe and O), or (b) reaction of wustite with inwardly diffusing oxygen to form a higher oxide at the free inside surface. The vapour pressure of iron at 600°C is only 2×10^{-12}Pa (2×10^{-17} atm) (Kubaschewski & Alcock, 1979) which is considered to be too low to provide adequate vapour phase transport of iron for (a) to be feasible. The oxygen pressure in the void above the metal surface (Figure 19) will initially be that in equilibrium with Fe and FeO, i.e. 1.3×10^{-20} Pa (1.3×10^{-25} atm) at 600°C, and so an oxygen concentration gradient exists across the oxide and oxygen with diffuse inwards. The p_{O_2} within the wustite layer will increase and only needs to rise by a factor of 4 to be

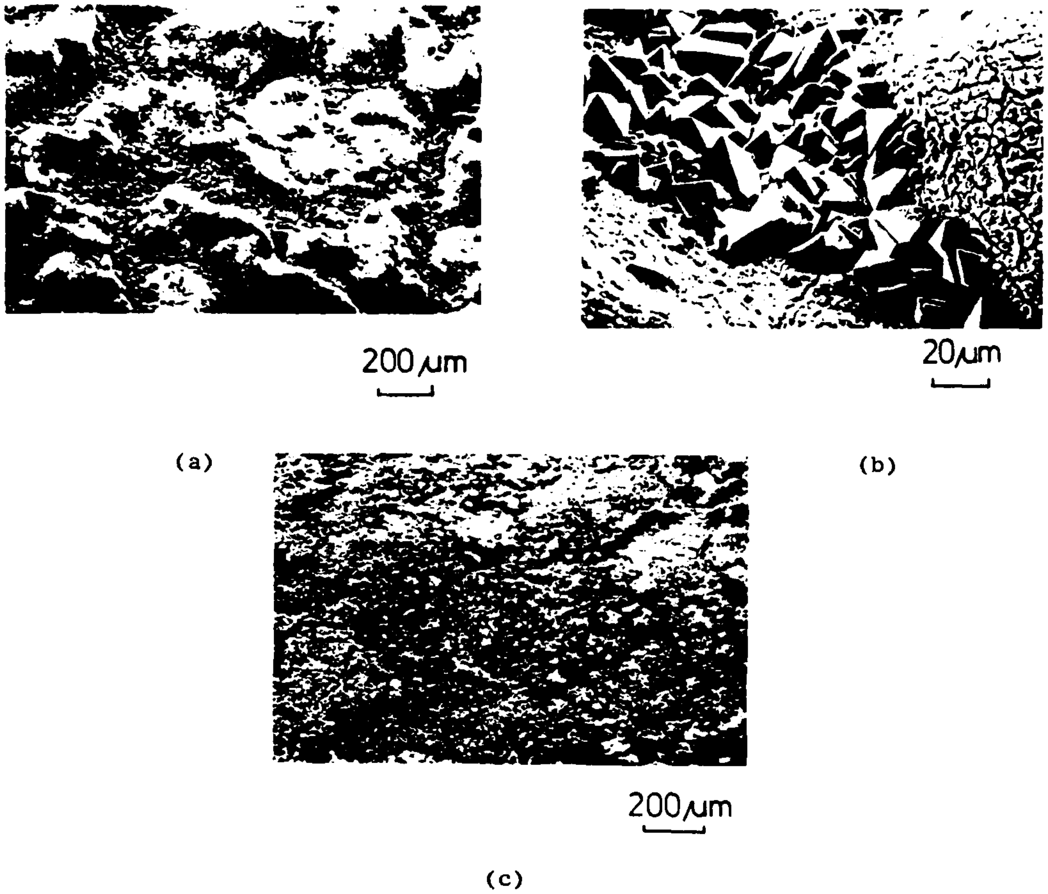


Figure 18. SEM micrographs of mild steel nitrided in $5NH_3:95H_2$ at 700°C and oxidised in air for 650h at 600°C. (a) and (b) underside of the oxide, (c) surface of the metal

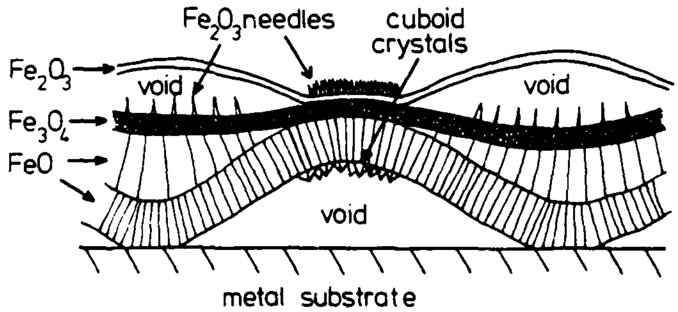


Figure 19. Schematic diagram of the oxide formed on nitrided mild steel oxidised in air for 650h at 600°C

in equilibrium with FeO and Fe_3O_4 at 600°C (5×10^{-20} Pa = 5×10^{-25} atm). When the local p_{O_2} close to the oxide/void interface reaches this value magnetite will form and grow with a geometric morphology as it forms at a free surface. Similar arguments hold if wustite oxidises to the higher oxide haematite. The crystallites formed on the underside of the oxide have not been positively identified. Their presence and the relatively oxide-free smooth metal surface below the voids, indicate that the oxygen pressure within the voids remains very low during oxidation. If cracking of the oxide occurs with subsequent gas penetration at atmospheric pressure, the metal surface would be expected to oxidise rapidly and fill the void with oxide. This is not observed, implying that the oxide layer does not crack. Such observations show that the effect of nitriding on the oxidation behaviour of these alloys is to produce a very compact oxide scale which is able to accommodate not only growth stresses but also those stresses generated during cooling.

II.3 Conclusions

High-temperature oxidation resistance of ferritic iron alloys is improved by a nitriding treatment which produces a dispersion of incoherent particles. A fine-grained oxide scale is formed which has a higher fracture strain than the coarser oxide which forms on annealed alloys, and no void formation occurs at the oxide/metal interface. The improved cohesion and adhesion of the oxide on nitrided and aged alloys is, however, not reflected in the results of thermogravimetric studies. The reduced interfacial voidage on the dispersoid-containing alloys allows unrestricted cation transfer from metal to oxide and although the interfacial adhesion is improved, the oxidation conditions are insufficiently aggressive to cause spalling on un-nitrided alloys and so no obvious benefit of improved adhesion is observed by weight gain measurements. Experiments on nitrided mild steel oxidised at 600°C demonstrate the resistance to fracture of oxides formed on nitrided alloys. A convoluted multi-layer oxide is formed which remains intact throughout 650h oxidation at 600°C and subsequent cooling to room temperature.

The resistance of nitrided austenitic iron alloys to aqueous corrosion is shown by potentiokinetic measurements to be greater than that of the corresponding annealed alloys. Similar behaviour has also been demonstrated for ferritic alloys in report J79. This behaviour is not understood but is not simply related to oxide nucleation and cohesion as is the case in high-temperature oxidation. This is evident from the remarkable corrosion resistance of nitrogen-alloyed Nitronic 50 and its marked decrease when nitrogen is removed from solid solution. In the solution treated alloy no precipitates are present and resistance to general and pitting attack is therefore due only to nitrogen in solid solution. It should be noted however that while the nitrogen-containing steel is fully austenitic (see Figure 20; Cr equivalent = 23.8, Ni equivalent = 24.4), after denitriding

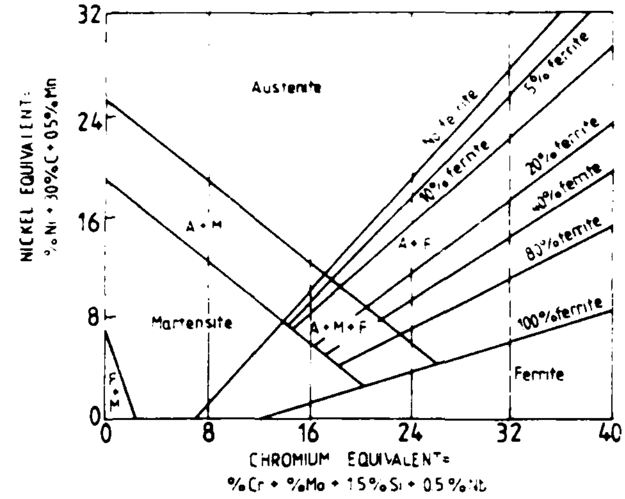


Figure 20. Schaeffler diagram for austenitic stainless steels

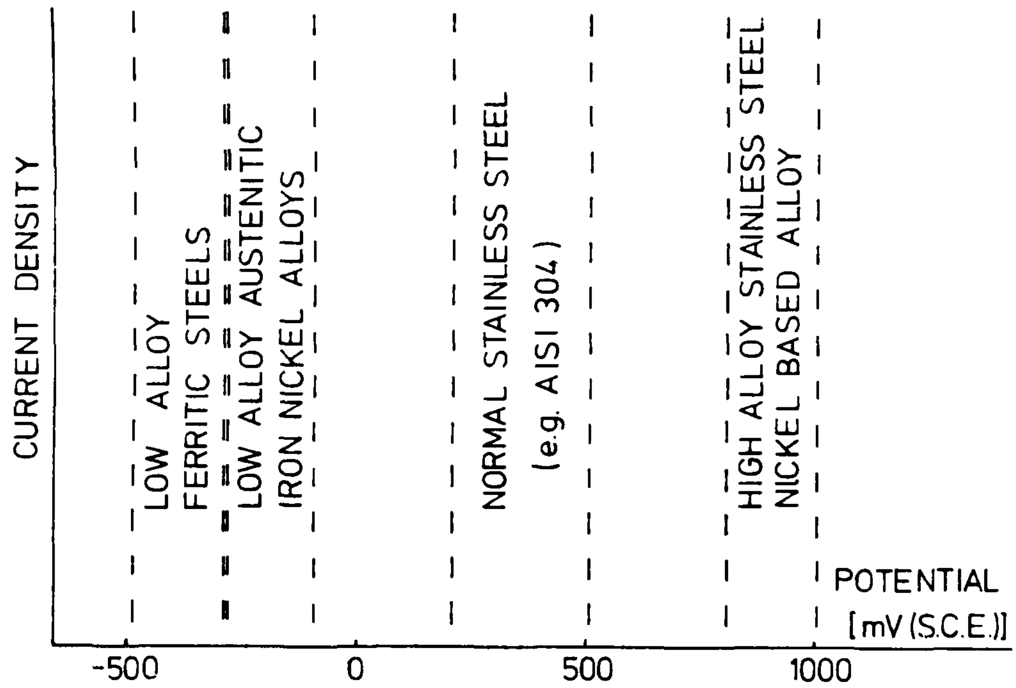


Figure 21. Pitting corrosion potentials for various types of steels

(Cr equivalent = 23.8, Ni equivalent = 17.0) approximately 5% of ferrite may form, possibly resulting in grain boundary corrosion.

Chen & Stephens (1979) have shown that a 12w/o Cr steel can be produced with anodic polarisation characteristics comparable to AISI 304 (18w/o Cr, 8w/o Ni, 2w/o Mn) by suitable alloying with Ni, Si, Al and Mo. From the present work it is reasonable to suggest that by adjustment of, for example, the manganese content to increase the nitrogen solubility to 0.2 - 0.3w/o, then the Cr concentration could be reduced below 12w/o without impairing the corrosion resistance typical of AISI 304. The effect of nitrogen is to increase the potential at which pitting occurs and Figure 21 shows the potential regions, relative to a saturated calomel electrode, at which pitting occurs for different alloy groups. Addition of 0.1 - 0.3w/o nitrogen makes the potential for pitting more positive by 0.1 - 0.2 volts. The same improvement without nitrogen would require several weight percent of expensive metal alloying additions.

The results substantiate the initial observation that nitrogen in iron alloys improves the resistance to aqueous corrosion but the improvement is insufficient to impart appreciable resistance to water in simple ferrous alloys. Even an austenitic Fe-34w/o Ni alloy containing molybdenum or titanium, although improved by nitriding, will still rust in tap water.

III. REFERENCES

Chen, W.Y.C. & Stephens, J.R., 1979 Corrosion, 35, 443.

Coates, D.J. & Hendry, A., 1979 Metal Science, 13, 315.

Driver, J.H., Sinclair, R. & Jack, K.H., 1979 Proc. Roy. Soc., A367, 99.

Driver, J.H., Unthank, D.C. & Jack, K.H., 1972 Phil. Mag., 26, 1227.

Hartline, A.C., 1974 Met. Trans., 5, 1974.

Hendry, A., 1978 Corrosion Science, 18, 555.

Hochman, J., 1977 Mater. et Techn., 69.

Howes, V.R., 1968 Corrosion Science, 8, 221.

Howes, V.R., 1969 J. Electrochem. Soc., 116, 1286.

Jack, K.H., 1974 Metal Science, 8, 271.

Jack, K.H., 1975 "Heat Treatment '73", London, The Metals Society, pp. 39-50.

Jack, K.H., 1979 Semi-annual Report "The Oxidation and Corrosion Resistance of Nitrided Iron Alloys" European Research Office, U.S. Army (DAERO-79-G-0035).

Janik-Czachor, M., Lunarska, E. & Szklarska-Smialowska, Z., 1975 Corrosion, 31, 394.

Kubaschewski, O. & Alcock, C.B., 1979 "Metallurgical Thermochemistry" 5th Ed., Oxford, Pergammon.

Mallick, K.K., 1979 M.Sc. Thesis, University of Newcastle upon Tyne.

Steenslund, O., 1969 Iron and Steel, 42, 104.

Tien, J.K. & Pettit, F.S., 1972 Met. Trans., 3, 1587.

Truman, J.E., Coleman, M.J. & Pirt, K.R., 1977 British Corr. Journal, 12, 236.

Turkdogan, E.T. & Ignatowicz, S., 1958 J.I.S.I., 188, 242.

IV. ADMINISTRATIVE ACTIONS

1) Information has been exchanged and discussions held with Dr. R.J. Weiss of the Army Materials & Mechanics Research Center, Watertown, and with Dr. R. Quattrone of the European Research Office, London.

   A series of alloys designed to save chromium but to be comparable, after nitriding, with commercial stainless steels was received from Dr. R.J. Weiss. Termination of the contract prevented any exploration of their oxidation and corrosion resistant properties.

2) Copies of the first Semi-Annual Report on "The Oxidation and Corrosion Resistance of Nitrided Iron Alloys" (DAERO-79-G-0035) were sent to Professor A. Crowell, University of Vermont, and to Professor R. Kaplow, Massachusetts Institute of Technology. In correspondence with these workers the number, size and shape of specimens required for their studies were established.

3) The specification of samples sent to Professor Crowell and to Professor Kaplow on 20th March 1980 and 4th July 1980 are given in Appendix 1.

4) Notice of termination of the contract on 31 March 1980 was received on 1 April 1980.

V. ANNEX

(a) The following statement shows the funds allocated, spent and overspent on the contract at the end of the report period i.e. at the end of the contract on 31 March 1980

(rate of exchange, £1 = $2.20)

	U.S. dollars		
	allocated	spent	overspent
Salaries			
B. Mortimer	15,808	18,447	2,639
Technical assistance	4,254	4,254	-
	20,062	22,701	2,639
University Overheads			
20% salaries	4,012	4,540	528
Reports	300	500	200
Other costs	600	660	60
Total	24,974	28,401	3,427

In addition to this overspending of $3,427 (= £1,558) the cancellation of the contract by E.R.O. without prior warning or notification on 1 April 1980 meant that Dr. B. Mortimer had to be retained in employment for a further three months. This involved a further deficit expenditure of $5,570 (= £2,532).

The total deficit on the contract, borne by the Crystallography Laboratory was therefore $8,997 (= £4,090).

(b) No property was acquired during the report period with Grant funds.

VI. APPENDICES

A1

Data Sheet for unnitrided and nitrided iron alloys sent to Professors Crowell and Kaplow, March 1980.

To: Professor Crowell - 5 specimens 20mm x 10mm x 0.55mm of each of 6 alloys A-F

To: Professor Kaplow - 3 specimens 20mm x 10mm x 0.5mm of each of 6 alloys A-F

I. Fe:0.48w/o Ti (ferritic)

A. unnitrided, annealed in vacuum at 850°C for 30 minutes.

B. annealed as A, nitrided at 580°C in $8.5NH_3:91.5H_2$ for 18 hours, Nitrogen content 0.29w/o.

C. annealed and nitrided as B, i.e. nitrided at 850°C in $8.5NH_3:91.5H_2$ for 18 hours, Nitrogen content 0.28w/o, then hydrogen reduced (pure H_2) at 500°C for 19 hours. Final Nitrogen content 0.15w/o.

II. Fe:35w/o Ni:0.50w/o Ti (austenitic)

D. unnitrided, annealed in vacuum at 850°C for 30 minutes.

E. annealed as D, nitrided at 700°C in $10.0NH_3:90.0H_2$ for 46 hours, Nitrogen content 0.22w/o.

F. annealed and nitrided as E, i.e. nitrided at 700°C in $10.0NH_3:90.0H_2$ for 41 hours, Nitrogen content 0.21w/o, then hydrogen reduced (pure H_2) at 600°C for 20 hours. Final Nitrogen content 0.17w/o.

Note

The specimens are through-nitrided so that surfaces can be prepared and polished at MIT and Vermont to meet the requirements of different examinations. Specimens A and D can, of course, be heated in vacuum at up to 850°C without change. C and F can be heated in hydrogen at up to respectively 500° and 600°C. B and E lose "excess" nitrogen, i.e. the nitrogen not held in monolayer clusters with titanium, when heated in hydrogen above about 300°C for long periods. This "excess" nitrogen is also precipitated slowly as α''-$Fe_{16}N_2$ by heat-treatment below 300°C but only after long times that obviously depend again on temperature. At 200°C, for example, there is incomplete precipitation after 100 hours, and so there might be some change in surface properties. It should be emphasized that the "clustered" nitrogen (0.15w/o for specimens B and C; 0.17w/o for E and F) is remarkably stable and is precipitated as TiN only by long overaging at temperatures above 600°C.

AII

Data Sheet for unnitrided and nitrided iron sent to Professors Crowell and Kaplow, July 1980.

To: Professor Crowell - 5 specimens 20mm x 10mm x .5mm of each of three pure iron alloys (G) - (I).

To: Professor Kaplow - 3 specimens 20mm x 10mm x .5mm of each of three pure iron alloys (G) - (I).

High purity iron supplied by INCO Europe Limited and prepared by vacuum induction melting and casting:

Heat No. 4142-1

Analysis, w/o

Ti	Mn	Nb	Mn	Si	Cu
0.02	0.02	0.02	0.02	0.03	0.02
Cr	Ni	Mo	C	N	O
0.02	0.03	0.02	0.003	0.0005	0.008

(G) unnitrided, annealed in vacuum at 940°C for 25 minutes; see electron micrograph (G), x 80,000.

(H) annealed as G, nitrided at 585°C in $8NH_3:92H_2$ for 20 hours; quenched, aged at room temperature;
see electron micrograph (H), x 80,000, showing nitrogen clusters; nitrogen content from weight gain, 0.06w/o.

(I) as H, then aged at 250°C for 6 hours;
see electron micrograph (I), x 20,000, showing γ'-Fe_4N precipitates.

DAT

FILM